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## NOVEL SYNGAS-BASED PROCESS FOR METHYL METHACRYLATE

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### ABSTRACT

Research Triangle Institute (RTI), Eastman Chemical Company, and Bechtel are developing a novel process for synthesis of methyl methacrylate (MMA) from coal-derived syngas, under a contract from the U.S. Department of Energy, Pittsburgh Energy Technology Center. This three-step process consists of synthesis of a propionate, its condensation with formaldehyde, and esterification of resulting methacrylic acid (MAA) with methanol to produce MMA. Eastman has focused on the research on propionate synthesis step. The resultant Mo catalysts work efficiently at much less severe conditions (170 °C and 30 atm) than the conventional Ni catalysts (270 °C and 180 atm). Bechtel has performed an extensive cost analysis, which shows that Eastman's propionate synthesis process is competitive with other technologies to produce the anhydride. In the second step, RTI and Eastman have developed active and stable V-Si-P and Ta metal oxide catalysts for condensation reactions of propionates with formaldehyde. RTI has demonstrated a novel correlation among the catalyst acid-base properties, condensation reaction yield, and long-term catalyst activity. Current research focuses on enhancing the condensation reaction yields, acid-base properties, in situ condensation in a high-temperature, high-pressure (HTHP) slurry reactor, and alternate formaldehyde feedstocks. Based on Eastman and RTI laboratory reactor operating data, a cost estimate is also being developed for the integrated process.

### INTRODUCTION

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MASTER

Methyl methacrylate (MMA) is an important high-value polymer intermediate used in plastic sheeting for signs, coatings, adhesives, fibers, and paints. Currently, about 4 billion pounds of MMA are produced worldwide and demand is growing. This demand cannot be met by U.S. plants because of the adverse environmental impacts of the dominant commercial technology, the acetone-cyanohydrin (ACH) process. There is a clear commercial opportunity for new processes, which are particularly attractive if they are based on domestic coal resources and are environmentally benign [1].

A new syngas-based process is being developed for the production of MMA. This process consists of three main steps—the synthesis of a propionate (C<sub>3</sub>) compound, its condensation with

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methanol-derived formaldehyde, and the esterification of the resulting methacrylic acid (MAA) with methanol to produce MMA. The first two steps represent the key technical challenges and are the focus of the project.

The first step, propionate synthesis, is focused on two tasks:

- Development of a homogeneous catalyst for propionate synthesis
- Preliminary design and economic analysis.

The second step, condensation of methanol-derived formaldehyde with the propionate, is also focused on two tasks:

- Development of an acid-base catalyst for condensation of formaldehyde with propionate
- Development of a combined methanol partial oxidation—acid-base catalyst for in situ oxidative condensation for one-step MMA synthesis.

## STEP 1. PROPIONATE SYNTHESIS

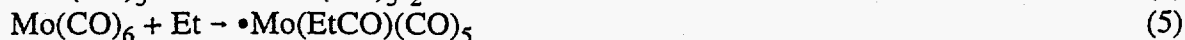
**Catalyst Development.** Eastman Chemical has developed a process for the conversion of ethylene and carbon monoxide to propionate derivatives (Equation [1]). The specific reaction product is dictated by the nature of the corresponding nucleophile (R).



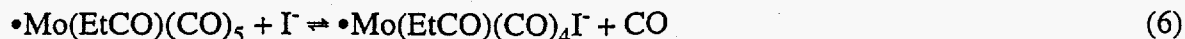
Intensive investigation of the process for the generation of propionic anhydride (R=Et), using  $\text{Mo(CO)}_6$  in conjunction with ethyl iodide and iodide salts, has revealed that the mechanism is likely a free radical one. This is based on the identification of trace amounts of coupled propionyl products, significant inhibition by duroquinone, and the observation of half-order dependencies on the Mo and EtI levels. The temperature dependence suggests that the rate limiting step is the dissociation of CO from  $\text{Mo(CO)}_6$ .

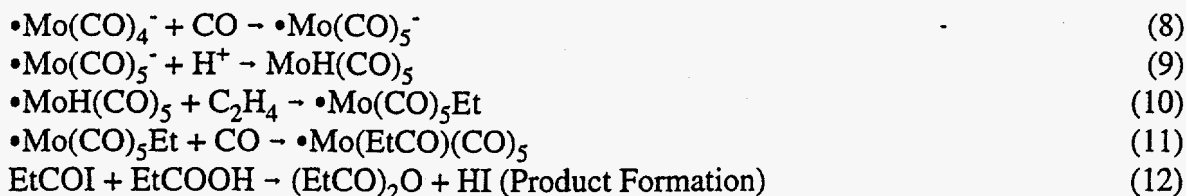
The reaction is kinetically independent of ethylene pressure, greater than inverse first order in CO, and first order in halide salt. (A small amount of hydrogen is also added to reduce Mo whose oxidation by EtI apparently initiates the radical chain process.) A mechanism that is consistent with these observations is as follows:

### *Initiation* (Catalyst Generation/Activation)

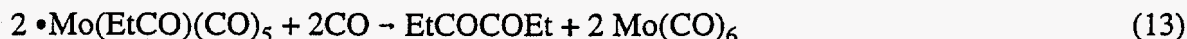


### *Propagation* (Catalytic Process)

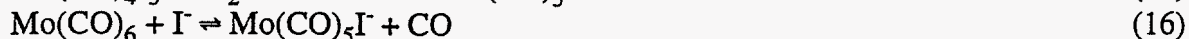
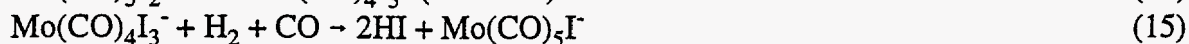




#### **Termination** (Catalyst Deactivation)



#### **Catalyst Regeneration** (Reduction of Mo(II) by Hydrogen)



**Process Economics.** Bechtel has performed a preliminary plant design and economic analysis of Eastman's novel technology for the synthesis of propionic anhydride. A simplified process flow diagram of this design is shown in Figure 1. Purified syngas from a modern coal gasification plant (i.e., Shell) is compressed, mixed with ethylene and propionic acid feed, and fed to the carbonylation reactor. Most of the hydrogen from the syngas was removed via a membrane separation unit, with only about 5 mol% remaining in the CO feed as a reducing agent for the catalytic system. The ethylene carbonylation reaction is carried out at 180 °C and 760 psig. Conversion is assumed to be 99% for ethylene, 96% for CO, and 70% for propionic acid.

The reaction product is taken from the reactor, depressurized to about 35 psig in a low-pressure flash evaporator. The bottom product is recycled. The propionic anhydride is separated from the unreacted propionic acid and byproducts. Unconverted propionic acid is recycled. Ethyl propionate was assumed to be the only significant byproduct and ethyl iodide the only significant organic halide catalyst component. Both are recycled back to the carbonylation reactor where the ethyl propionate is eventually reacted to form propionic anhydride. Unconverted gases are scrubbed with part of the fresh propionic acid feed, followed by water, before they are vented.

The process design (Figure 1) is based on a plant capacity of 250 million lb/yr of MMA from propionic anhydride with an assumed 95% yield from the in situ oxidation/condensation reaction. The propionic anhydride purity is 97 wt%. Propionic acid is the major impurity in the product.

The estimated total inside battery limits (ISBL) capital cost for this 330 million lb/yr propionic anhydride plant is about \$21.0 million (1992 \$, including 35% contingency). It is based on U.S. Gulf Coast material and labor rate, consistent with SRI's cost estimates for the various existing MMA processes [2]. Using SRI's methodology for offsite costs, utility cost estimation, and financial assumptions, the production cost of propionic anhydride via ethylene carbonylation is estimated at \$0.43/lb.

## **STEP 2. CONDENSATION CATALYSIS**

**Condensation of Propionate With Formaldehyde.** A key goal of this research is to find a stable and selective catalyst for the condensation of propionic acid and anhydride with formaldehyde. Based on reaction mechanism, both acid and base sites are needed for the condensation reaction

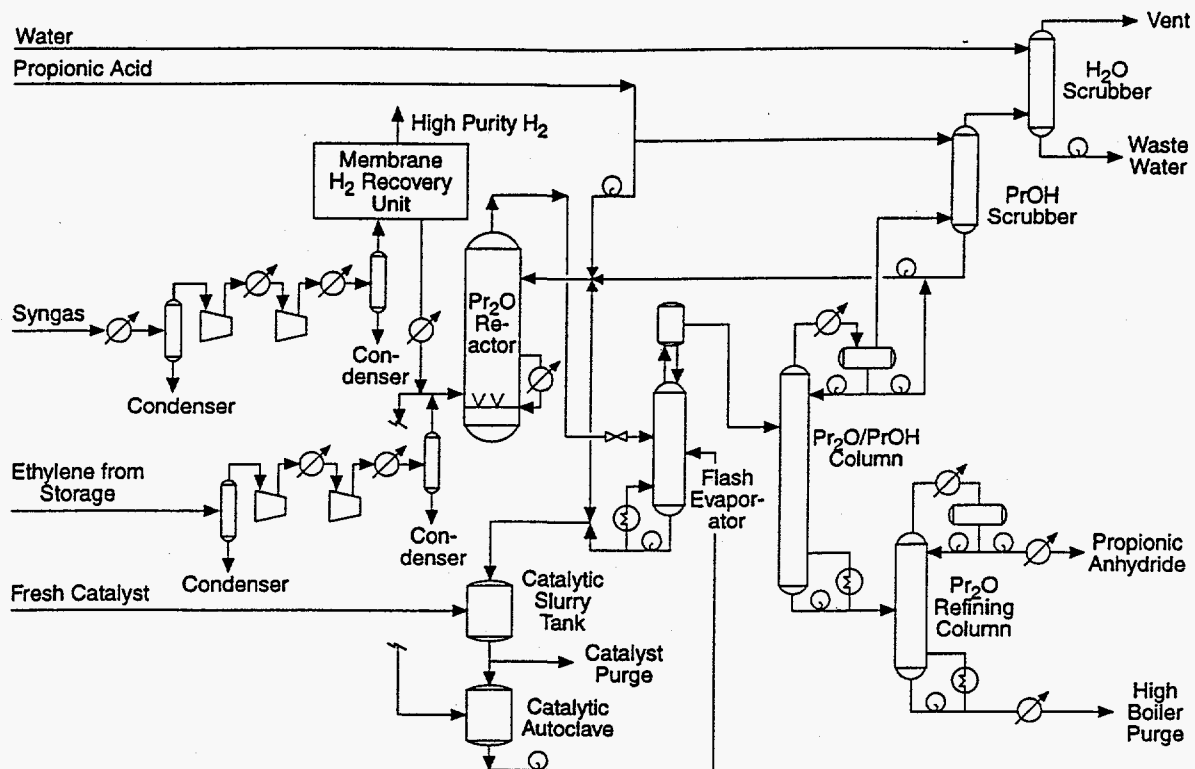


Fig. 1. A simplified process flow diagram for propionic anhydride synthesis.

to occur and a balance of acid-base strengths is needed for maximizing the condensation yields. Although vapor phase condensation of propionic acid and formaldehyde has been studied before [3,4], yields and selectivity to the desired product have been poor. Over 45 acid-base properties have been tested at Research Triangle Institute (RTI) laboratories for the vapor phase condensation reactions. Further details on catalyst synthesis, characterization, and testing have been shown elsewhere in these proceedings [5].

Two catalysts (V-Si-P 1:10:2.8 and Ta-Si 1:10) were chosen for a long-term deactivation study. The long-term deactivation pattern of the V-Si-P and Ta-Si is shown in Figure 2. The deactivated catalyst was treated at 300 °C, in a mildly oxidizing atmosphere, with 2% oxygen in nitrogen as the treatment gas. [Hydration of the surface did not restore activity.] The activity of the catalyst was checked following this regeneration. The MAA yield was restored to 40.8%. This suggests that the deactivation was due to coke formation on the catalyst surface. The Ta-Si catalyst shows greater stability with time-on-stream than the V-Si-P catalyst (Figure 2) although the initial yields of MAA are similar for these two catalysts. Because the condensation reaction is catalyzed by the acid and base sites on the catalyst surface, these properties were measured using temperature-programmed desorption (TPD) of  $\text{NH}_3$  (for the acid sites) and  $\text{CO}_2$  (for the base sites)[6,7]. The rapid deactivation of the V-Si-P catalyst may be caused by its stronger acidic surface. The acid-base properties, initial condensation activity, and long-term deactivation are being explored further to develop a stable condensation catalyst. This has led to a novel catalyst which looks commercially promising. This catalyst is currently being patented. The long-term stability studies

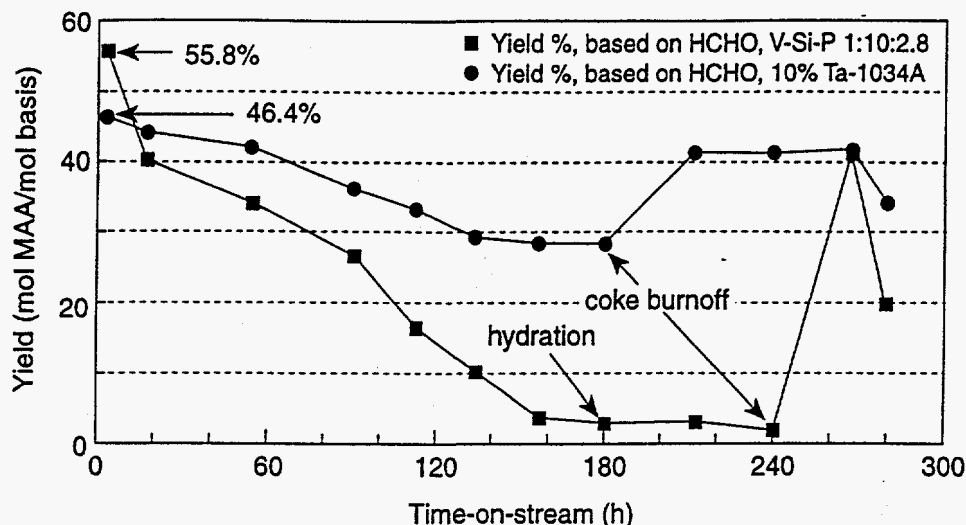


Fig. 2. Long-term deactivation of V-Si-P and Ta-Si.

have also indicated that thermal deactivation (by sintering or catalyst agglomeration) may also be responsible for accelerating coke formation. Because heat transfer in the laboratory fixed-bed reactors is considerably poorer than industrial type pilot-scale reactors, a slurry reactor is better suited for these highly exothermic condensation reactions in industrial practice.

***In Situ Oxidative Condensation Studies.*** Using the catalysts developed for condensation of propionate with formaldehyde from the aforementioned research, RTI has demonstrated the in situ oxidative condensation of methanol with a propionate in a fixed-bed microreactor system. The in situ oxidative condensation occurs over a physical mixture of a methanol partial oxidation catalyst and a propionate condensation catalyst. Methanol, oxygen, and propionate are fed over a bifunctional catalyst at 300 °C, 2 atm, and 290 to 1,200 cc/g cat·h space velocity. The reaction product is MMA and MAA. The maximum yield of MMA from in situ studies at these reactor conditions is 9.9%, based on charged methanol. These are the first reported results of a successful in situ oxidative condensation study. To demonstrate the principle in a high-temperature, high-pressure (HTHP) slurry reactor, RTI has designed, assembled, and operated an HTHP slurry system for in situ oxidative condensation studies (see Figure 3).

## CONCLUSIONS

***Propionate Synthesis.*** A novel Mo-based homogeneous catalyst technology for the synthesis of the propionate feedstock has been developed by Eastman. Bechtel has completed the preliminary plant design and economic analysis for this technology, and results show that it is competitive with other conventional routes for propionate synthesis via ethylene hydroformylation.

***Condensation Catalysis.*** Novel V-Si-P ternary catalysts and Ta-silica catalysts that exhibit higher condensation yields have a characteristic high q-ratio. The acid-base property study suggests that a low surface acidity with a high q-ratio coupled with an effective reactor heat removal scheme may be best for a commercial catalyst. RTI has designed, assembled, and demonstrated the operation of an HTHP slurry reactor system for in situ oxidative condensation studies. These are the first ever reported results of successful in situ production of MMA.

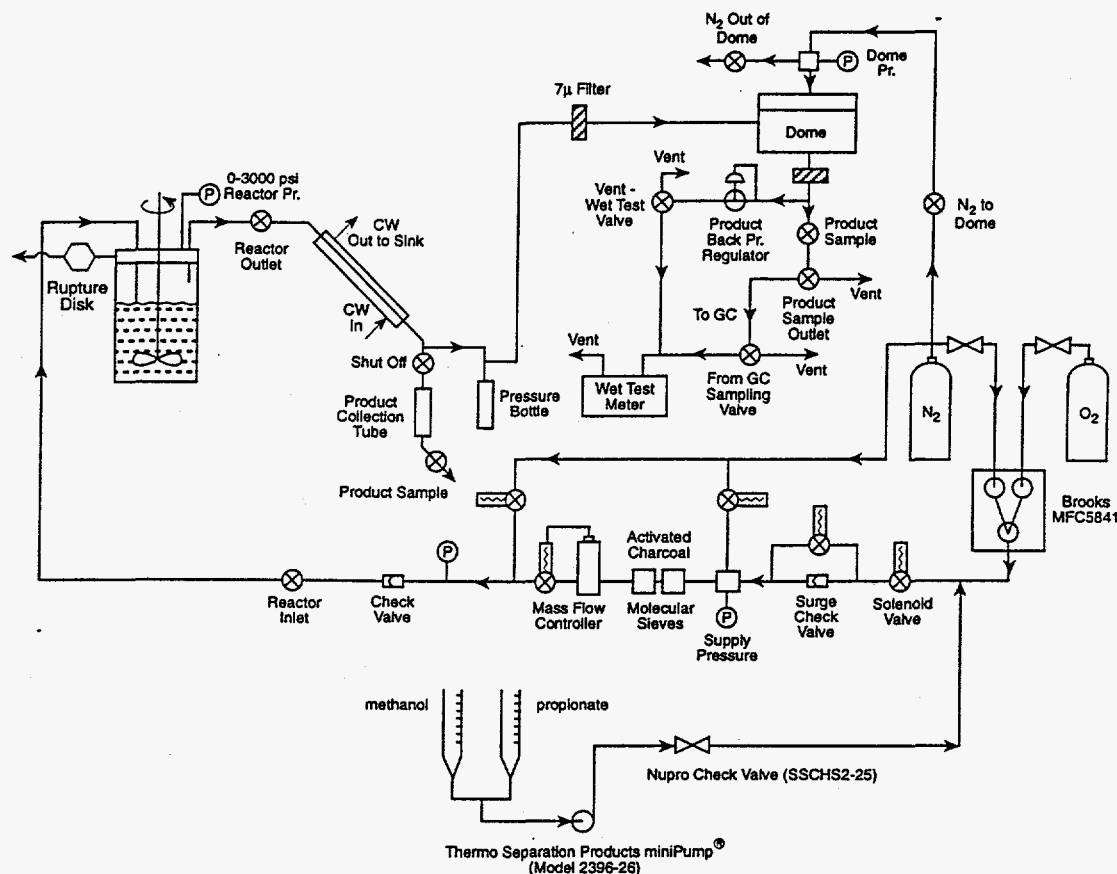


Fig. 3. Schematic of RTI-Eastman slurry reactor system.

## ACKNOWLEDGEMENTS

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